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ENGLISH TRANSLATION DOCUMENT

The following attached document is the English Translation Document for the below referenced Chinese patent application.

Application Date: 2003 04 14

Application Number: 03 1 14242.7

Application Type: Invention

Title: Compounds of Lithium Nickel Cobalt Metal Oxide and Their Methods of Fabrication

Applicant: BYD LTD.

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Attorney Docket: BYD-US2003-008

Translation Certification

I hereby certify that the following translation of the respective certified copy is correct.


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Compounds of Lithium Nickel Cobalt Metal Oxide and Their Methods of Fabrication

Abstract

A type of compound of lithium nickel cobalt metal oxide and its method of fabrication.

5 The chemical formula of said lithium nickel cobalt metal oxide compound is $\text{Li}_{\alpha}\text{Ni}_{1-b-c}\text{Cob}_{\beta}\text{M}_{\gamma}\text{O}_2$ where $0.97 \leq \alpha \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, and M is one or more or the following: manganese, aluminum, titanium, chromium, magnesium, calcium, vanadium, iron, and zirconium. The ingredient of said material, lithium cobalt hydroxy compound, M compound, and lithium compound, is ballground to uniformly mix and then 10 calcined twice to obtain said material. This invention, the $\text{Li}_{\alpha}\text{Ni}_{1-b-c}\text{Cob}_{\beta}\text{M}_{\gamma}\text{O}_2$ material has a higher degree of crystallization and good electrochemical properties.

Specification

Compounds of Lithium Nickel Cobalt Metal Oxide and Their Methods of Fabrication

Field of Invention

5 This invention relates to the material for the positive electrode of a type of anhydrous rechargeable battery and its method of fabrication. Particularly, it relates to a type of compound of lithium nickel cobalt metal oxide and its method of fabrication.

Background of Invention

In recent years, with the widespread use of a variety of portable electronic products, 10 lithium ion rechargeable batteries with its many superior characteristics such as high voltage, large specific capacity, low self-discharge, and zero memory effects, have been highly favored. The positive material used in lithium batteries are mainly embedded type compounds. At present, the material for the positive electrode with the best overall properties is lithium cobalt material, LiCoO_2 .
15 However, the LiCoO_2 material is expensive and its source scarce. Therefore, people have suggested using compounds of lithium manganese oxides or compounds of

lithium nickel oxides as substitutes for the LiCoO_2 material. The compounds of lithium manganese oxides have the problem of having a lower theoretical capacity. In addition, the range of the decrease of its capacity during repeated charging and discharging or under higher temperature is larger.

5 On the other hand, even though the compounds of lithium nickel oxides do not possess the same disadvantages as the compounds of lithium manganese oxides, LiNiO_2 possesses the same crystal structure as LiCoO_2 and its properties are worse than that of LiCoO_2 . This is because the Ni^{3+} ion, as compared with the Co^{3+} ion, more easily revert back into the Ni^{2+} ion. Since the size of the Ni^{2+} ion and the Li^{+} ion are similar, 10 ($r\text{Ni}^{2+} = 8.7\text{nm}$, $r\text{Li}^{+} = 9.0\text{nm}$), the Ni^{2+} ion and the Li^{+} ion can easily substitute each other, forming the halite magnetic domain that has inactive electrochemical property, resulting in the lowering of a battery's capacity.

In preparing the $\text{LiNi}_{(1-y)}\text{Co}_y\text{O}_2$ material, people have generally use the calcination method on a mixture of compounds of lithium, nickel, and cobalt.

15 The article in Chen, Express, 6, 161191 provided a method to fabricate a type of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ material: mix together $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and LiOH solution. Initially

dry this mixture at 90°C, then heat treat at 800°C in air to produce the product.

Japan Patent Publications 2000-058053 discloses the composition method for a type of $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ material. Calcine a predetermined ratio of a mixture of lithium, 5 cobalt, and nickel salts in dried atmosphere without carbon dioxide at 300°C to 700°C for over 2 hours. Grind. Then calcine again at 700°C to 900°C to obtain the desired material.

Other than this, since, under higher temperature, the Ni^{3+} ion easily reverts back into the Ni^{2+} ion, people also first oxidizes the Ni^{2+} ion to become the Ni^{3+} ion, then 10 calcine to react the mixture at lower temperatures to fabricate the $\text{LiNi}_{(1-b)}\text{Co}_b\text{O}_2$ material.

Chinese Patent Publications CN1142691A provides a method of heat treating at 400°C to 500°C the initial ingredients, oxides containing cobalt, hydroxide compounds of nickel, $\text{Ni}_{1-y}\text{Co}_y\text{OOH}$, and a type of lithium compounds, to fabricate the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ material.

15 The above described method for the fabrication of the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ material all have the disadvantages of insufficient crystallization, non-uniform structure, and

insufficiently large specific surface area resulting in poor electrochemical properties for the active material for positive electrodes.

Description of Invention

The object of this invention is to provide a type of compound of lithium nickel cobalt oxide compound with high degree of crystallization, complete crystalline shapes and good electrochemical properties.

The object of this invention is implemented through the following technology plan.

A type of compound of lithium nickel cobalt metal oxide whose chemical formula is $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ where $0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, and M is one or more or the following: manganese, aluminum, titanium, chromium, magnesium, calcium, vanadium, iron, and zirconium. In its X-ray diffraction picture ($\text{CuK}\alpha$), the ratio of the intensity of its peak on its (003) crystalline surface, and the intensity of its peak on its (104) crystalline surface, I_{003}/I_{104} is larger than 1.20.

In order to prevent the formation of the halite magnetic domain, other metal elements, such as cobalt, manganese, or iron etc. can be used to partially replace nickel.

Among these, the lithium nickel cobalt oxide compound $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ using cobalt as the

replacement exhibits still more excellent overall properties.

The material's X-ray diffraction picture (CuK α) can be used to examine whether there is halite magnetic domain formation by examining the ratio of intensity of its diffraction peak on its (003) crystalline surface, and the intensity of its diffraction peak on 5 its (104) crystalline surface, I_{003}/I_{104} . In general, when $I_{003}/I_{104} >$ than 1.20, then the material fundamentally does not have halite magnetic domain formation.

The fabrication method of a type of compound of lithium nickel cobalt metal oxide that includes the following steps:

- (1) The fabrication of cobalt nickel hydroxy compound: add ammonia to a 10 uniformly mixed solution of cobalt sulfate and nickel sulfate to form the cobalt nickel hydroxy compound, its formula representation is $Ni_{1-b}Co_b(OH)_2$.
- (2) Compounds of lithium nickel cobalt metal oxide:
 - (a) First calcination: Ballgrind and mix evenly predetermined quantities calculated from the chemical formulae the following: lithium compound, said 15 $Ni_{1-y}Co_y(OH)_2$, and M compound. Calcinate in oxygen atmosphere at between 600°C and 720°C for 1 to 10 hours;

(b) Second calcination: Calcinate the product from step (a) in oxygen atmosphere at 750°C to 900°C for 8 to 20 hours.

(c) Cool product from step (b) rapidly, ballgrind, sift to obtain the compound of lithium nickel cobalt metal oxide with the chemical formula $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$.

5 In order to compensate for the vaporization during the high temperature calcination process, a preferred specification for step (2) is to add appropriate amounts of additional lithium compound. In formulating the amounts of the reaction material needed, the ratio of Li/(Ni+Co+M) should be ensured to be between 1.01 and 1.10.

A preferred specification for step 2(a) and step (2)b is for the oxygen atmosphere 10 to be approximately one atmosphere.

The advantage of this invention is that positive electrodes using the material $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ fabricated by this invention exhibits excellent properties. The decrease in electrical capacity after repeated charges and discharges is small. The change in discharge voltage is also very small. At the same time, the formation of halite 15 magnetic domain is avoided.

The following attached figures of embodiments further explain this invention.

Description of Attached Figures

Figure 1 is the scanning electron micrograph of the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ material fabricated by this invention magnified 2000 times.

Figure 2 is comparison between the X-Ray diffraction picture (CuK α) picture of 5 the material for positive electrodes made with embodiments and comparison examples described below.

Figure 3 are graphs showing the changes in specific capacity following charging and discharging cycles of positive electrode material made with embodiments and comparison examples.

10 This invention provides the fabrication method of a type of material and the material, a type of $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ where $0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, and M is one or more of the following: manganese, aluminum, titanium, chromium, magnesium, calcium, vanadium, iron, and zirconium. The appearance of this $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ material is shown in Figure 1.

15 In order to obtain material for the positive electrode where the metal ions are distributed evenly and reduce the redistribution during the combination reaction of nickel

and cobalt, this invention uses the cobalt nickel hydroxy compound fabricated by adding ammonia to a uniformly mixed solution of cobalt sulfate and nickel sulfate. The formula of its structure is $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$. The advantage of using cobalt nickel hydroxy compound is that the cobalt nickel hydroxy compound can be fabricated to be spherically shaped. Provided that the process of fabricating the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ material does not destroy the spherical shapes, spherical shaped material can be obtained. This process not only produces products with better shapes, it also controls the desired granule diameter of the needed material product by controlling the granule diameter of the cobalt nickel hydroxy compound.

10 The lithium compound used in the reaction can be compound such as lithium hydroxide, lithium peroxy-oxide, lithium carbonate, and lithium nitrate. From the standpoint of the cost, customarily, lithium carbonate is used.

Mix uniformly the cobalt nickel ball, lithium compound, and M compound in predetermined ratio. Calcine in two steps under high temperature. First calcine at 15 600°C to 720°C for 1 hour to 10 hours to decompose the nickel balls and oxidize the Ni^{2+} ion. Then calcine again at 750°C to 900°C for 8 hours to 20 hours to complete the

growth process of the crystalline granules of $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$.

Since Ni^{3+} ion reverts back to Ni^{2+} ion at temperatures higher than 600°C, therefore, oxygen atmosphere is needed to control the progress of this reaction. Experiments show that the calcination process should proceed in oxygen pressure of approximately 1 5 atmosphere.

In formulating the reaction mixture, in order to compensate for the volatilization of lithium during high temperature calcination, adequate amounts of lithium compound have to be added. However, since the reaction cannot be calcined at overly high temperatures or overly long time periods, excessive amounts of lithium compound can lead to the 10 existence of contamination in the product. Therefore in formulating the reaction material, the ratio of $\text{Li}/(\text{Li}+\text{Co}+\text{M})$ should be ensured to be between 1.01 and 1.10.

During the first calcination, since the specified temperature is above the melting point for commonly used lithium compounds such as lithium hydroxide, lithium carbonate, and lithium nitrate, therefore the lithium compound is in melted form. In order to avoid 15 the existence of domains with missing lithium and domains rich with lithium, the concentration of the reaction material should not be over 5 centimeters.

$\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ has different structures at high and low temperatures.

Moreover, only the hexagonal layered halite structure at high temperature has

electrochemical properties. Therefore, rapid cooling is required to retain high

temperature phase structure of the product.

5 The compound of lithium nickel cobalt metal oxide fabricated by the method of this invention has average granule diameter between 1 μm and 20 μm . Its BET specific surface is between 0.2 m^2/g and 1.0 m^2/g .

Embodiment 1

Ballgrind to mix the cobalt nickel hydroxy compound $\text{Ni}_{0.81}\text{Co}_{0.19}(\text{OH})_2$ with 10 granule diameter between 8 μm and 10 μm and 5.2 times molar equivalent of lithium carbonate. Spread the mixture into a 2 cm thin layer and calcine at 650°C in oxygen atmosphere for 6 hours. Then calcine again at 800°C for 16 hours to fabricate the $\text{LiNi}_{0.81}\text{Co}_{0.19}\text{O}_2$ positive electrode material.

Embodiment 2

15 The difference with Embodiment 1 is: this embodiment uses the mixture

$\text{Ni}_{0.81}\text{Co}_{0.19}(\text{OH})_2$, manganese dioxide and lithium acid in the molar ratio of 0.95:0.05:0.52

to fabricate the $\text{LiNi}_{0.77}\text{Co}_{0.18}\text{Mn}_{0.05}\text{O}_2$ positive electrode material.

Embodiment 3

The difference with Embodiment 1 is: this embodiment uses the mixture

$\text{Ni}_{0.81}\text{Co}_{0.19}(\text{OH})_2$, aluminum hydroxide and lithium acid in the molar ratio of

5 0.95:0.05:0.52 to fabricate the $\text{LiNi}_{0.77}\text{Co}_{0.18}\text{Al}_{0.05}\text{O}_2$ positive electrode material.

Comparison Example 1

The fabrication method is the same as Embodiment 1. The difference is that in

this embodiment, the reaction system is placed in air.

Comparison Example 2

10 The fabrication method is the same as Embodiment 1. The difference is that in

this Embodiment, the reaction material is the mixture of nickel hydroxide, tri-cobalt

tetra-oxide and lithium carbonate in the molar ratio of 0.81:0.06:0.52.

Comparison Example 3

Mix nickel hydroxide with granule diameter between $8\mu\text{m}$ and $10\mu\text{m}$ and lithium

15 carbonate in the molar ratio of 1:0.52. Calcine mixture at 750°C in air for 6 hours to

obtain LiNiO_2 positive electrode material.

“Halite magnetic domain” experiment

A Japanese Science Company (Rigaku) product, model number D/MAX

2200PC, style XRD, is used to experiment with X-ray diffraction picture (CuK α) on the

material for the positive electrode products from the embodiments and comparison

5 examples. The specifications for the experiment are: Using Cu as the target and setting the

voltage as 40kV and the current as 20mA, the experiments obtained the X-ray diffraction

picture as shown in Figure 2. In Embodiments 1 through 3, the ratio of the intensity of

the diffraction peak on the (003) crystalline surface, I_{003} , to the intensity of the diffraction

peak on the (104) crystalline surface, I_{104} , I_{003}/I_{104} , is > 1.20 thus allowing the conclusion

10 that the materials basically do not have the “halite magnetic domain” formation. In

Comparison Examples1 through 3, the ratio of the intensity of the diffraction peak on the

(003) crystalline surface, I_{003} , to the intensity of the diffraction peak on the (104)

crystalline surface, I_{104} , I_{003}/I_{104} , is < 1.20 thus allowing the conclusion that the materials

have the “halite magnetic domain” formation.

15 Charging and Discharging Experiments

Mix together 90% by weight each of the above described six types of material for

the positive electrode, 4% by weight acetylene black and 4% by weight of polyvinyl flourine and use N-methyl pyrrolidone as the dispersant to fabricate the positive electrode compound. Heat dry at 150°C in vacuum to completely evaporate the N-methyl pyrrolidone and obtain the positive electrode compound. Press together the positive 5 electrode compound with a circular lithium net and heat at between 170°C and 180°C in vacuum for 4 hours to form positive electrode slice. Use circular lithium metal slice as the negative electrode, a mixture of ethyl carbonate and di-methyl carbonate containing 1 m of LiPF₆ as the electrolyte material to form a battery with a three electrode system. Charge and discharge the battery with 1mA/cm² to test its cycle characteristics. Please 10 refer to Figure 3.

Table 1

The Structure and Electrochemical Properties of Different Positive Electrode

Material

Experiments	Materials for the Positive Electrode	I ₀₃ /I ₁₀₄	Initial Discharge Specific	Specific Discharge Capacity after
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			Capacity/mAh/g	100 cycles /mAh/g
Embodiment 1	$\text{LiNi}_{0.81}\text{Co}_{0.19}\text{O}_2$	1.37	180	166
Embodiment 2	$\text{LiNi}_{0.77}\text{Co}_{0.18}\text{Mn}_{0.05}\text{O}_2$	1.33	176	168
Embodiment 3	$\text{LiNi}_{0.77}\text{Co}_{0.18}\text{Al}_{0.05}\text{O}_2$	1.34	175	167
Comparison Example 1	$\text{LiNi}_{0.81}\text{Co}_{0.19}\text{O}_2$	1.11	174	133
Comparison Example 2	$\text{LiNi}_{0.81}\text{Co}_{0.19}\text{O}_2$	1.15	175	145
Comparison Example 3	LiNiO_2	0.91	174	88

The data in Table 1 shows, the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ positive electrode material made from the fabrication method of this invention is superior to similar materials fabricated using convention methods, both in the structure of the compound and its electrochemical properties. They exhibit superior energy density and excellent charge and discharging cycle life characteristics. Also, this material has high economic value as the Co content is much less than that used in LiCoO_2 material for positive electrodes resulting in the

lowering of manufacturing cost.

Claims

1. A type of compound of lithium nickel cobalt metal oxide whose chemical formula is $\text{Li}_{\alpha}\text{Ni}_{1-\alpha}\text{Co}_{\beta}\text{M}_{\gamma}\text{O}_2$ where $0.97 \leq \alpha \leq 1.05$, $0.01 \leq \beta \leq 0.30$, $0 \leq \gamma \leq 0.10$, and M is one or more of the following: manganese, aluminum, titanium, chromium, magnesium, calcium, vanadium, iron, and zirconium. Its characteristics are, in its X-ray diffraction picture (CuK α), the ratio of the intensity of its diffraction peak on its (003) crystalline surface, and the intensity of its diffraction peak on its (104) crystalline surface, I_{003}/I_{104} is larger than 1.20.
- 10 2. The compound of lithium nickel cobalt oxide metal oxide of claim 1, its characteristics are: the average granule diameter of said compound of lithium nickel cobalt metal oxide is between $1\text{ }\mu\text{m}$ and $20\text{ }\mu\text{m}$, its BET specific surface area is between $0.2\text{ m}^2/\text{g}$ and $1.0\text{ m}^2/\text{g}$.
- 15 3. The fabrication method for said compound of lithium nickel cobalt oxide metal oxide of claim 1 or 2, its characteristics are: this method includes the following steps:

(1) The fabrication of cobalt nickel hydroxy compound: add ammonia to a uniformly mixed solution of cobalt sulfate and nickel sulfate to form the cobalt nickel hydroxy compound, its formula representation is $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$ compound.

(2) Oxides of lithium nickel cobalt metal compound:

5 (a) First calcination: Ballgrind and mix evenly predetermined quantities calculated from the chemical formulae the following: lithium compound, said $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$, and M compound. Calcinate in oxygen atmosphere at between 600°C and 720°C for one to 10 hours;

10 (b) Second calcination: Calcinate the product from step (a) in oxygen atmosphere at between 750°C and 900°C for 8 to 20 hours.

(c) Cool product from step (b) quickly, ballgrind, sift to obtain the compound of lithium nickel cobalt oxide metal oxide with chemical formula $\text{Li}_{a}\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$.

4. The fabrication method for said compound of lithium nickel cobalt oxide metal 15 oxide of claim 3, its characteristics are: in step 2(a), the ratio of $\text{Li}/(\text{Ni}+\text{Co}+\text{M})$ is between 1.01 and 1.10.

5. The fabrication method for said compound of lithium nickel cobalt oxide metal oxide of claim 3, its characteristics are: in step (2)a and step (2)b, the oxygen atmosphere is approximately one atmosphere.

5

6. The fabrication method for said compound of lithium nickel cobalt oxide metal oxide of claim 3, its characteristics are: during the calcination, the concentration of the reaction mixture is less than 5 centimeter.

10 7. The fabrication method for said compound of lithium nickel cobalt oxide metal oxide of claim 3, its characteristics are: after calcinations, the reaction mixture is rapidly cooled in dry air.

8. The fabrication method for said compound of lithium nickel cobalt oxide metal oxide of claim 3, its characteristics are: the molar content of Co in the ratio of Co/(Co+Ni+M) of said lithium nickel cobalt oxide metal oxide compound is between 1.0

and 0.30.

5

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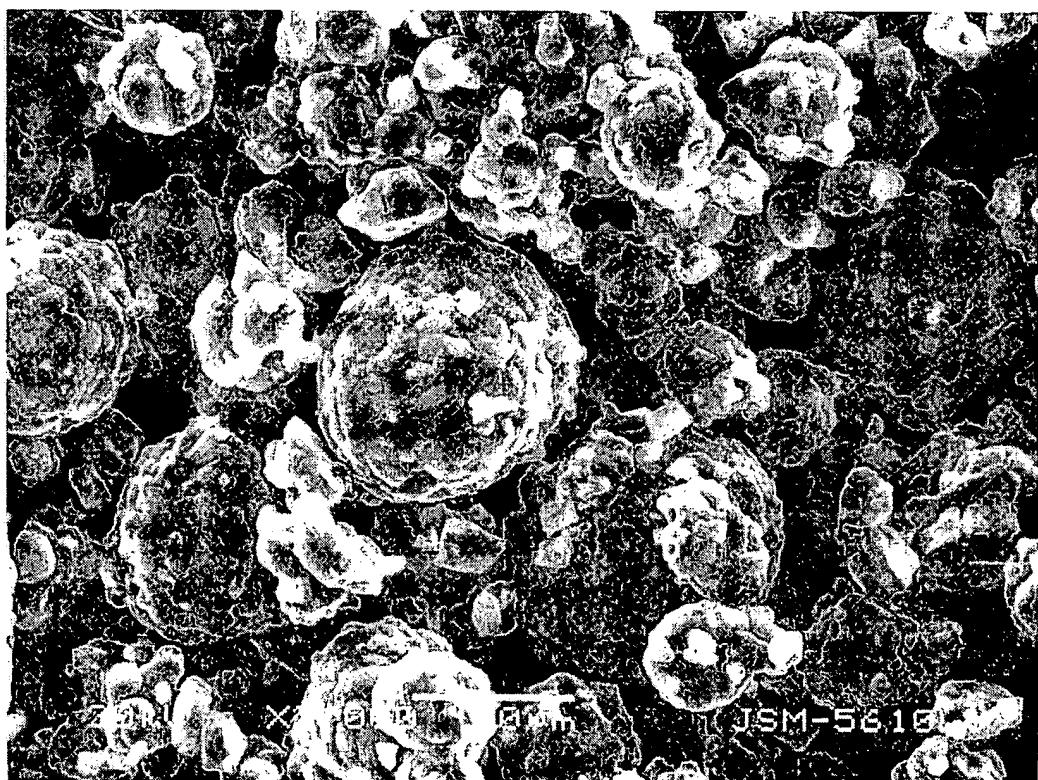


Figure 1

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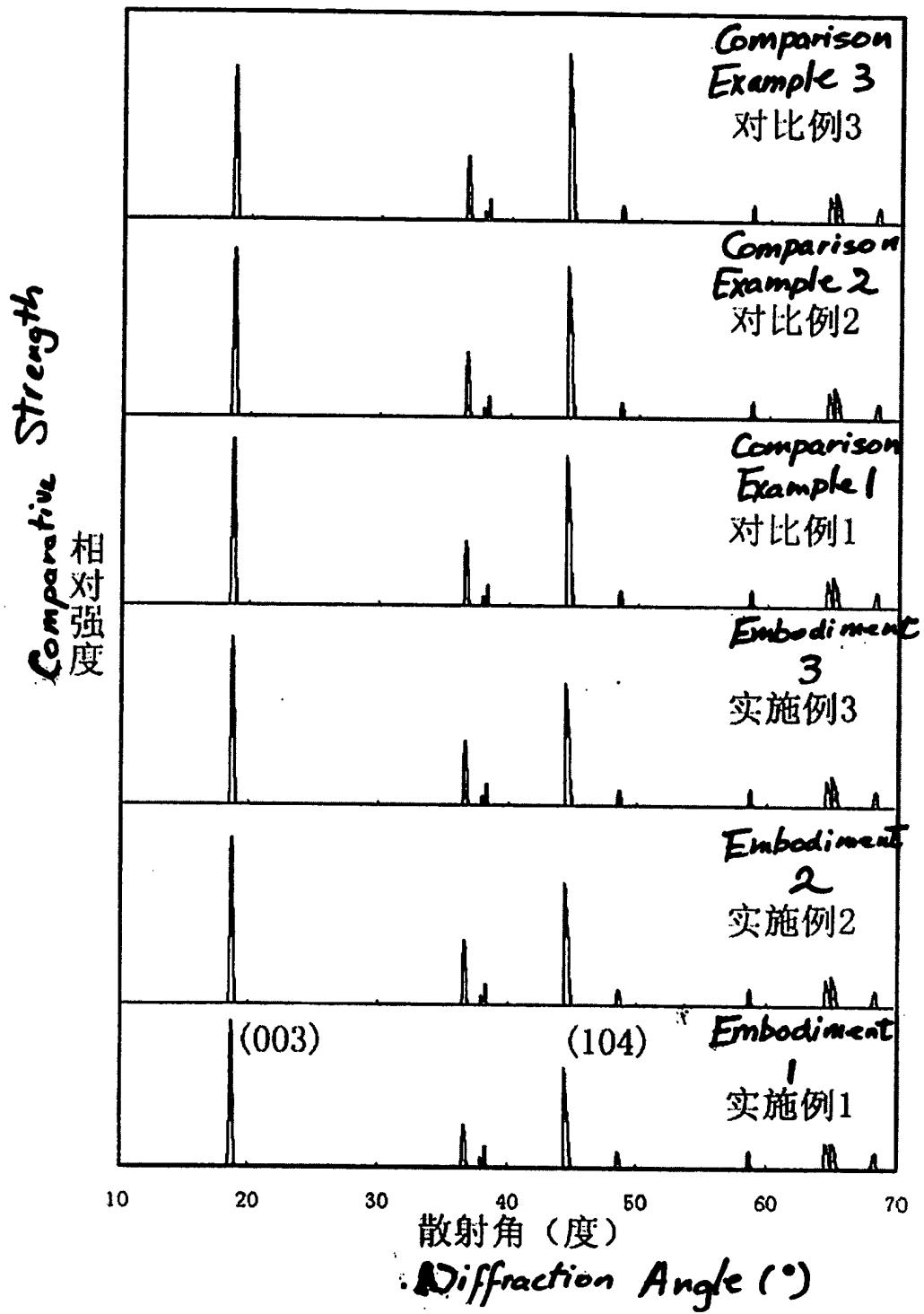


Figure 2

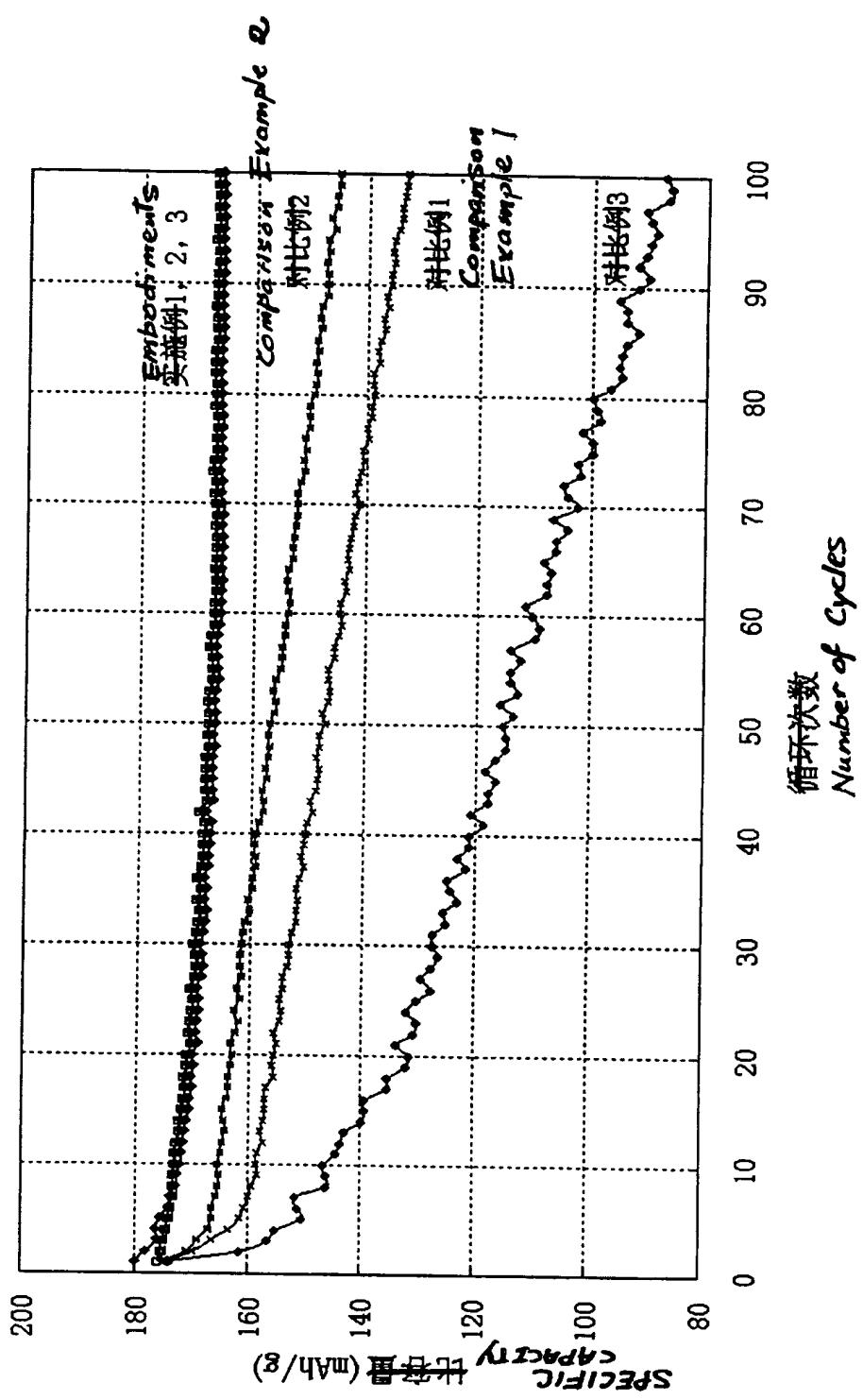


Figure 3